Segregation in desiccated sessile drops of biological fluids

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Abstract. It is shown here that concurrence between advection and diffusion in a drying sessile drop of a biological fluid can produce spatial redistribution of albumen and salt. The result gives an explanation for the patterns observed in the dried drops of the biological fluids.

PACS. 47.57.-s Complex fluids and colloidal systems – 47.55.nb Capillary and thermocapillary flows – 66.10.Cb Diffusion and thermal diffusion

1 Introduction

The dried droplets of the biological fluid have very complex structure. In particularly, there are protein ring at the periphery and dendritic crystals in the central area of the sample (Fig. 1). The visual appearance of a sample is used for diagnosing a wide range of diseases. Rather clear relationships of the 'pattern — pathological processes' type have been revealed [1].
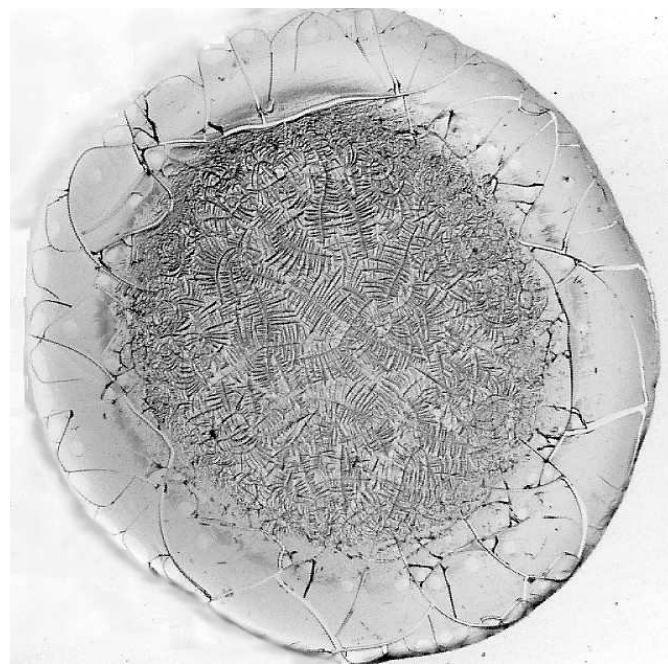

Fig. 1. A dried drop of the multi-component fluid consisting of NaCl (0.9 %), albumen (9 %), and water. This composition and the concentrations are typical for the blood serum of the healthy persons.

The priority in the investigation of the dehydration self-organization phenomenon in biological fluids belongs to Rapis [2]. While seeming simple, the effect turned out to be extremely complicated and to involve a number of interrelated processes of different nature.

The biological fluids are complex colloidal systems. Even the slightest variation in the composition of a liquid leads to total changes in the dynamics of phase transitions during drop drying [3]. Despite the application of the effect to practical medical diagnostics [1], and the drastic improvement of our understanding of pattern formation, complex non-linear dynamics of pattern formation in drops of biological fluids is mostly unclear. Nevertheless, the performed analysis allows to conclude that the main effects observed in the dehydration of biological fluids are typical for colloidal solutions in general and can be described in the framework of conventional approaches [4].

This work is an part of the research on mathematical modeling of pattern formation in a biological fluid upon desiccation, with a special emphasis to evaporation, capillary flow [5], effect of diffusion [6,7] and sol-gel phase transition. The main scientific goal of the research is determination the relationship between the pathological processes occurring in an organism, the variation of the physical and physicochemical properties of the biological fluids caused by these processes, and the kind of the patterns produced in the drying of the sessile droplet of a biological fluid. The results presented in this paper allow to give the fundamental explanation of spatial component redistribution as a consequence of diffusion and capillary flow.

2 Model

2.1 Theory of solute transfer

Detailed investigation of of solute transfer in the desiccated drops was performed by Deegan et al. [8]. In their
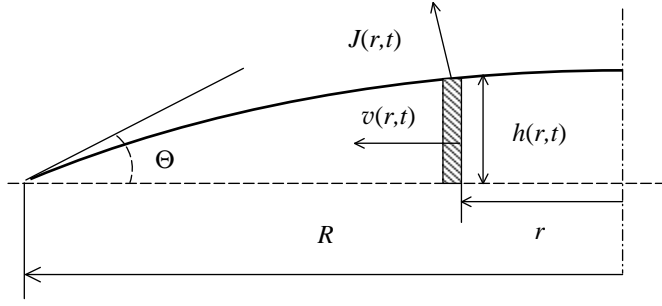
Fig. 2. Schematic of relevant parameters for the theory.

theory, an outward flow in a drying drop of liquid is produced when the contact line is pinned so that liquid that is removed by evaporation from the edge of the drop must be replenished by a flow of liquid from the interior. This flow is capable of transferring 100% of the solute to the contact line and thus accounts for the strong perimeter concentration of many stains. Furthermore, the theory relies only on a generic property of the substrate-solvent interaction, the presence of surface roughness or chemical heterogeneities that produce contact line pinning, and therefore it accounts for the ubiquitous occurrence of ring-like stains.

Indeed, as soon as evaporation begins, particles deposit onto the substrate, resulting in a strong anchoring of the three-phase line. In the case of biological fluid, proteins are adsorbed on the substrate, leading to a strong anchoring of the triple line.

Recently, segregation in multi-component ceramic colloids during drying of droplets was investigated [9].

If the size of the solute particles is small, diffusive currents become comparable to the advective currents [8].

Biological fluid widely used in the medical tests is blood serum. It consists of the proteins (mostly albumen) — about 9 %, NaCl — 0.9 %, and water. It is shown in this work, that concurrence between diffusive and capillary flows can produce more uniform distribution of salt along a drop diameter, but has not essential effect on albumen distribution.

The conservation of fluid determines the relationship [8] between the vertically averaged radial flow of the fluid, v, the position of the air-liquid interface, h, and the rate of mass loss per unit surface area per unit time from the drop by evaporation, J:

$$\frac{\partial}{\partial t}(\rho h) + \frac{1}{r}\frac{\partial}{\partial r}(r\rho h v) + J\sqrt{1 + \left(\frac{\partial h}{\partial r}\right)^2} = 0, \quad (1)$$

where ρ is the density of the liquid. All quantities are supposed to be dependent both of distance r, and of time t. For additional explanation see Fig. 2.

The flow velocity can be expressed from (1) by rewriting it in the integral form [8]

$$v = -\frac{1}{\rho r h}\int_0^r dr\left(J\sqrt{1 + \left(\frac{\partial h}{\partial r}\right)^2} + \rho\frac{\partial h}{\partial t}\right)r. \quad (2)$$

The conservation of solute gives

$$\frac{\partial}{\partial t}(\rho c h) + \frac{1}{r}\frac{\partial}{\partial r}(r\rho h c\tilde{v}) = 0, \quad (3)$$

where c is concentration, $\tilde{\mathbf{v}} = \mathbf{v} + \mathbf{v}_d$ is velocity including both advective term, $\mathbf{v}$, and diffusive one, $\mathbf{v}_d$, [10]. Here $c\mathbf{v}_d = -D\mathrm{grad}\,c$, where D is the diffusion constant for solute in solvent. Then

$$v_d = -\frac{D}{c}\frac{\partial c}{\partial r}. \quad (4)$$

Master equation describing spatial and temporal solute dynamics is

$$\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(rD\frac{\partial c}{\partial r}\right) +$$
$$\frac{\partial c}{\partial r}\left(\frac{D}{h}\frac{\partial h}{\partial r} + \frac{D}{\rho}\frac{\partial\rho}{\partial c}\frac{\partial c}{\partial r} - v\right) + \frac{cJ}{\rho h}\sqrt{1 + \left(\frac{\partial h}{\partial r}\right)^2}. \quad (5)$$

One needs to know the evaporation law, the drop profile, and the vertically averaged radial flow of the fluid inside the drop to solve the master equation.

2.2 Simplifying assumptions

We will suppose that

- air–liquid interface has a spherical cap shape induced by surface tension [8];
- drop apex height steadily decreases with constant velocity v_0: $h(0,t) = h_0 - v_0 t$, where h_0 is initial height of drop apex [11]; then $J = \rho v_0/2$;
- in a multicomponent fluid the components do not influence on each other;
- diffusion coefficient for each component D is constant;
- variation of the solution density ρ *vs.* concentration c is rather small, so we will suppose constant density everywhere, but the term containing $\partial\rho/\partial c$, because this term may be very large even for small variations of the density.

Detailed description of the main assumption can be found in Ref. [12].

2.3 Evaporation models

We could not find any experimental data about spatial distribution of vapor flux near the drop surface, the theoretical models are rather controversial and contradictory.

The analogy between diffusive concentration fields and electrostatic potential fields (they both satisfy Laplace's equation) is widely used for calculation of the vapor flux of a sessile droplet [8,13,14]. In particularly, this approach was used to describe the vapor flux of very thin evaporating droplets [12,15]. In this model, the evaporation flux is almost uniform all over free surface except very narrow region near the drop edge [13]. Nevertheless, there is a

singularity at the contact line. The divergence at the edge is nonphysical and can be removed by using a smoothing function [15].

An alternative method for determining the evaporative mass flux is to use heat transfer analysis [16]. Therefore, this form cannot be applied to a droplet in which the contact line is pinned because the presence of colloidal particles affects the evaporation near the edge [17]. To mimic this effect the evaporation function was modified [17].

On the other hand, there is a region near the contact line with high evaporation rate [18].

Following Ref. [19] the simplest possible kind of vapor flux is assumed in the present work, i.e. a constant evaporation rate all over free surface.

2.4 Dimensionless form of the master equation

Using above assumptions, one can rewrite master equation (5) in the dimensionless form

$$\frac{\partial c}{\partial \tau} = \frac{\mathbb{D}}{x}\frac{\partial}{\partial x}\left(x\frac{\partial c}{\partial x}\right)+$$

$$\frac{\partial c}{\partial x}\left(\frac{\mathbb{D}}{L}\frac{\partial L}{\partial x}+\frac{\mathbb{D}}{\rho}\frac{\partial \rho}{\partial c}\frac{\partial c}{\partial x}-kv\right)+\frac{kc}{2L}\sqrt{1+\left(\frac{\partial L}{\partial x}\right)^2}, \quad (6)$$

where $\mathbb{D} = h_0 D/(v_0 R^2)$ is dimensionless parameter, $\tau = tv_0/h_0$ is dimensionless time, $x = r/R$ is dimensionless distance, and $k = h_0/R$. $L(x,\tau)$ is dimensionless profile of the drop written as

$$L(x,\tau) = \sqrt{\left(\frac{A^2+1}{2A}\right)^2 - x^2} - \frac{1-A^2}{2A},$$

where $A(\tau) = k(1-\tau)$ and

$$B(x,\tau) = \sqrt{(A^2(\tau)+1)^2 - (2A(\tau)x)^2} - A^2(\tau) - 1.$$

The dimensionless velocity can be written as

$$v(x,\tau) = \frac{(A^2(\tau)+1)\left(\frac{B(x,\tau)}{2A^2(\tau)}+x^2\right)}{4A(\tau)xL(x,\tau)}.$$

3 Results and discussion

In medical diagnostics, drops of a biological liquid in volume 10–20 μl are used. The drops are placed onto the strictly horizontal glass. Thus diameter of a droplet is 5–7 mm and $h_0 \approx 1$ mm [1]. Hence, $k = 0.33$. Diffusion coefficients are $D_a = 7.7 \cdot 10^{-11}$ m²/sec (albumen) and $D_s = 1.5 \cdot 10^{-9}$ m²/sec (NaCl). Experiments on measurement of height of a drying up drop show, that $v_0 \approx 4 \cdot 10^{-7}$ m/sec [20]. Then dimensionless parameters are $\mathbb{D}_a \approx 0.03$ (albumen) and $\mathbb{D}_s \approx 0.6$ (NaCl). We suppose that salt has no effect on solution density because of very small concentration. Then density of solution is linear function of albumen concentration $\rho(c) = 1000 + 300c$ kg/m³ and $\frac{1}{\rho}\frac{\partial \rho}{\partial c} = 0.3$ [21].

Equation (6) was solved numerically. Presented in Fig. 3 results show that diffusive processes can prevent carrying out of salt on edge by capillary current. At the same time, diffusion has not essential influence on spatial distribution of albumen. As a result the edge of a sample consists mainly from albumen, while its central part is composed both from salt and from albumen. This result confirms qualitative conclusions obtained earlier using simplest model [6,7]. One can see that near the drops edge there is rather narrow region with high concentration of albumen. Phase transition of albumen from sol to gel have to occur in this region.

4 Acknowledgments

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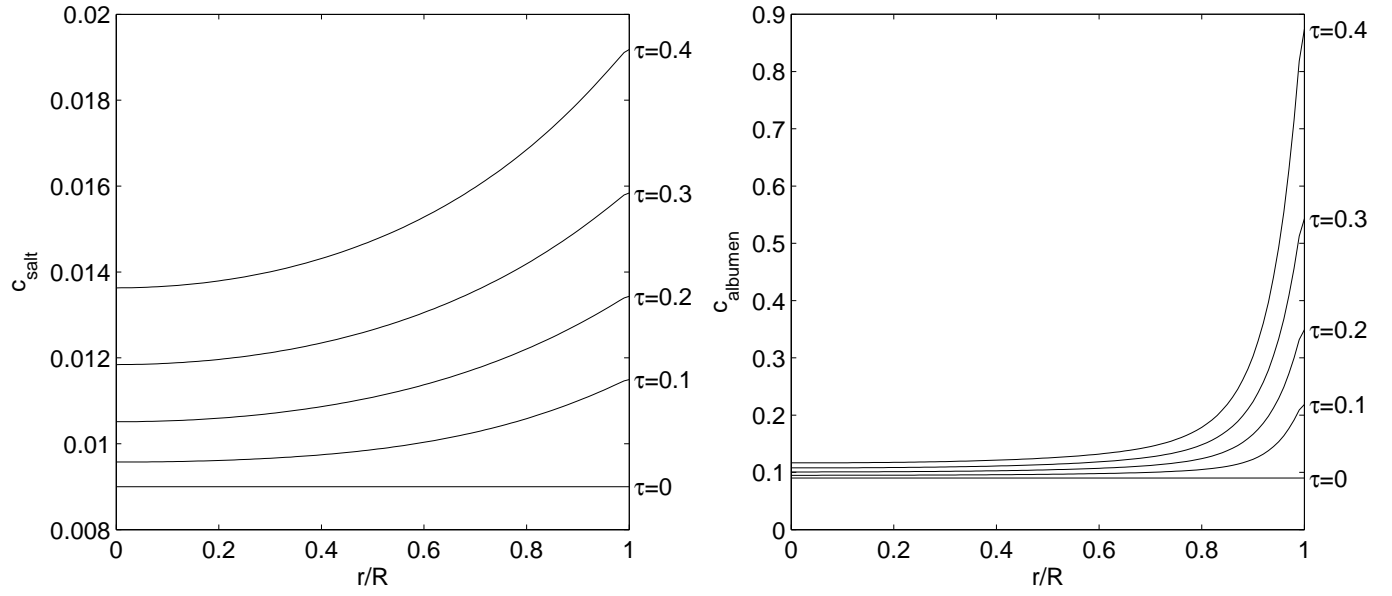21. H. Chick, C. J. Martin, Biochem. J. **007**, 92 (1913)

Fig. 3. Dynamics of the spatial distribution of the components inside a desiccated drop of biological fluid.